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Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair and Assembly

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Composite Vehicle Research Center

Michigan State University

Project ID # : LM087

MICHIGAN STATE UNIVERSITY | Composite Vehicle Research Center

OVERVIEW

TIMELINE

- **Start Date:** October 1, 2013
- **End Date:** September 30, 2016
- Percent Complete – 15%

BUDGET

- **Total Project Funding:** $599,999
- **Funding Received in Budget Period 1: (10/2013-12/2014) :** $156,088
- **Funding for Budget Period 2: (01/2015 – 12/2015) :** $207,282

BARRIERS ADDRESSED

- **Joining and Assembly**
  - **Light-weight, reversible bonded joints**
- **Performance**
  - **Enhanced damage resistance of joints using nanomaterials**
- **Predictive Modeling Tools**
  - **Development of Experimentally Validated Simulations.**

Partners / Collaborations

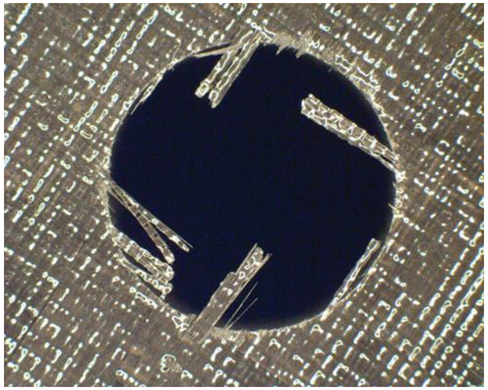
- **Eaton Innovation Center, MI.**

Project Lead

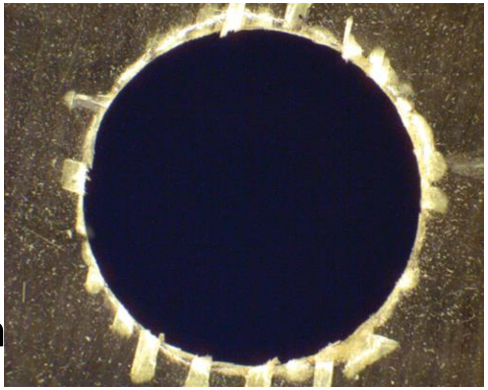
- **Composite Vehicle Research Center (CVRC), Michigan State University,**

Introduction / Relevance ; Joining

- **JOINING**
  - Joining is inevitable, allows versatility in assembly and repair, reduces manufacturing costs and time.
  - Considered a 'weak-link' in the structure due to complex phenomena and interactions
  - Classification: Temporary vs. Permanent Joints
- **Mechanical Fastening** (Source: Cloud G, SEM 2012)
  - Oldest, most important type of joining, over 200 billion industrial fasteners used in USA.
  - Approximately 18,000 fasteners are used in F-18 aircraft
  - Fasteners cost ~ 1/3 of the airplanes, same as engines.
  - Repair and Re-assembly is the biggest advantage!
- **Limitations / Challenge**
  - Fasteners add to significant structural weight!
  - Machining holes in composites cause delaminations, strength reduction and, in general introduce stress concentrations

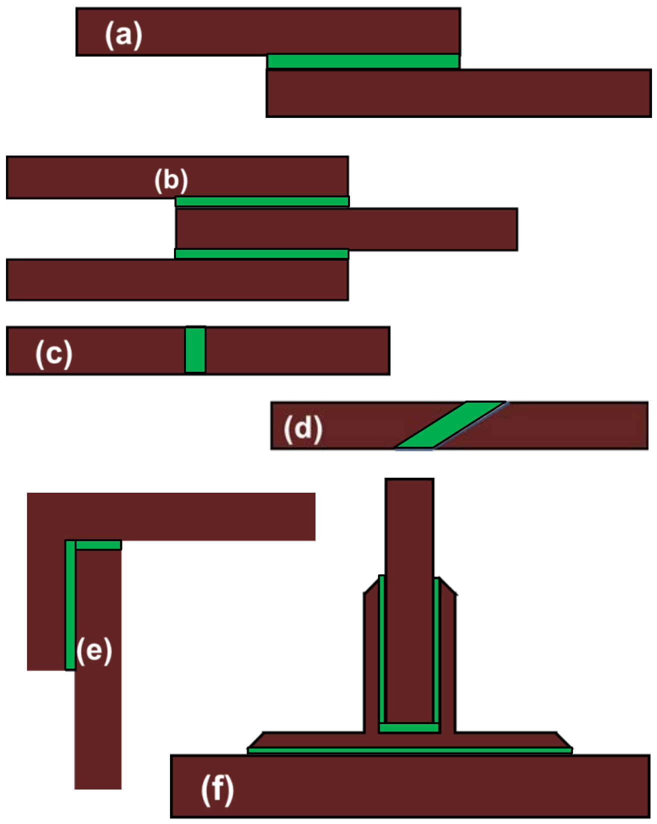


Delamination in composites due to hole-drilling, Gardiner, Composites World , (2012)



Introduction/ Relevance - Joining

- **Adhesive Joining**
  - Potential reduction in Weight & Cost
  - Preferred over mechanical fastening
  - Eliminates stress-concentrations and strength reduction due to holes
  - Lack of confidence in using all bonded structures
- **Common Practices**
  - Most commonly used structural adhesives are one-time cure.
  - In general, disassembly, repair and re-assembly is not feasible.
- **Challenge**
  - Multi-Use, Repair and Reassembly?

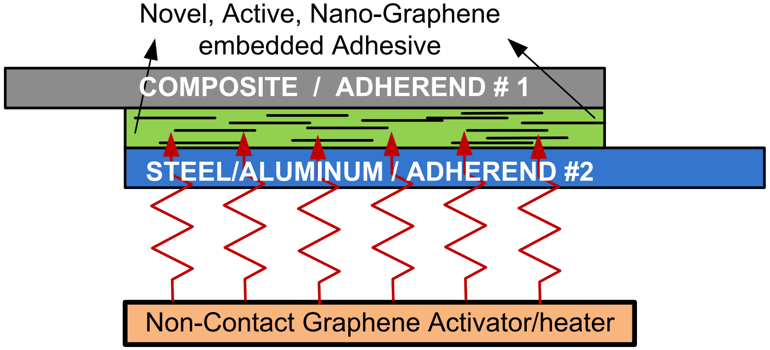


Types of Adhesive Joints

a) Lap-Joint
b) Double Lap-Joint
c) Butt Joint
d) Scarf Joint
e) Corner/L-joint
f) T-/Pi- Joint

Global Objective(s) & Approach

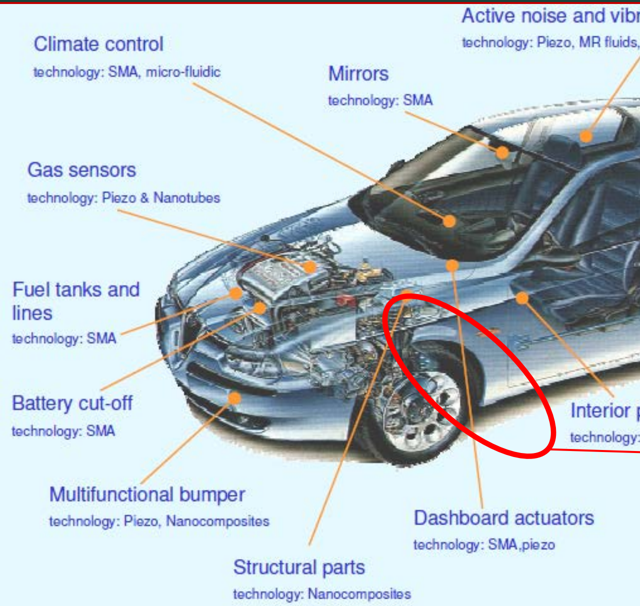
- **OBJECTIVE**
  - To demonstrate the feasibility of ACTIVE Adhesive technology for structural joining of similar / dissimilar adherend materials.
- **ACTIVE ADHESIVES**
  - Thermoplastic adhesives reinforced with conductive nano-graphene (GnP) platelets
  - Allow targeted heating of adhesive only using interaction of microwaves and graphene.



Schematic of the concept shown for in-plane joints

- **APPROACH**
  - An integrated experimental and numerical approach that would eliminate costly trial-and-error, instead use a rational computational materials (materials by design) based approach. Multi-use, Repair & Reassembly?
  - Synergistic use of Non-Destructive Evaluation Tools for joining efficiency and health monitoring.

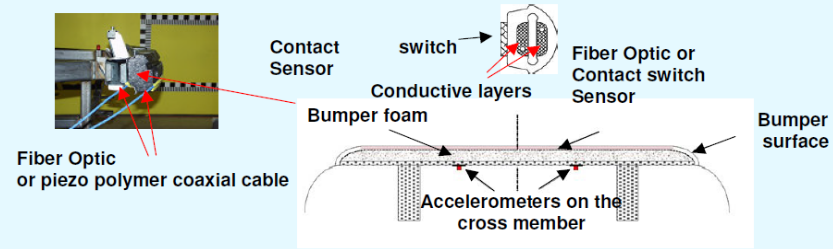
Milestones and Relevance



Koricho (2012, PhD Thesis, Politechnico Di Torino)

Some known composites and plastics materials in Automotive sector:

- ***GFRP***
- ***CFRP***
- ***GMT***
- ***SMC***
- ***PA***
- ***PA 66***
- ***PP***



Available solution based on "add-on" approach

	Milestone	Type	Description	Status
FY 14	Activation and Bonding	Technical	The novel active adhesive couples with microwave radiations to activate, bond/un-bond resulting similar joints	Success / In-Progress
	Structural Properties Defined	Go / No-Go	The novel active adhesive structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	Success
FY 15	Demonstration of Structural Properties	Technical	The structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	
	Proven Efficiency	Technical	The NDE techniques used can prove the efficiency of the activation and re-assembly/bonding of the resulting joints	
	Characterization of Material Properties	Go / No-Go	The experimental characterization of material properties of the adhesive and adherend can be successfully performed to provide input to robust simulations (next phase)	

Objective(s) & Approach -I

- **OBJECTIVE**
  - The overall objective of 'active adhesive' development will be achieved by following sub-tasks:
- **A. Processing, Material Development and Optimization of Active Adhesive**
  - To Determine Processing Parameters of graphene nanoplatelets (GnP), choice of thermoplastics, evaluating optimal content of GnP to achieve synergy of multi-functional properties (e.g., stiffness-toughness balance) and activation adhesives for re-assembly and repair.
- **B. Lab-Scale Evaluation and Detailed Material Characterization**
  - To utilize strategically selected experiments to:
    - (i) evaluate the material properties of the adhesives and the adherends.
    - (ii) characterize multi-material lap-joint properties as per ASTM standards,
    - (iii) evaluate the re-assembly/repair of joints using novel NDE tools such as embedded sensors and IR thermography, and
    - (iv) utilize low-cost, liquid molding techniques to develop fiber-reinforced composite adherends.

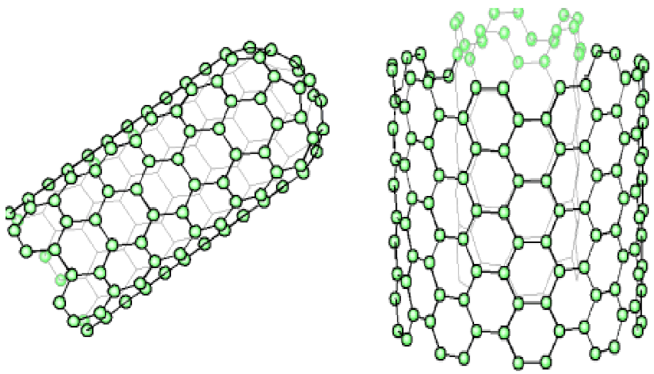
Objective(s) & Approach -II

- **OBJECTIVE**
  - The overall objective of 'active adhesive' development will be achieved by following sub-tasks:
- **C. Development of Design Tools and Database**
  - To develop robust experimentally validated simulations (EVS) that can be used
    - (i) to predict the material designs and behavior of joints beyond the experimental matrix studied, and
    - (ii) as a design tool and database development for other joints with high reliability and confidence
- **D. Large-scale Structural Joining & Industrial Applications**
  - To experimentally evaluate the behavior of large-scale (realistic/industry-relevant) multi-material joints in:
    - (a) in-plane mode (lap-joints),
    - b) out-of- plane mode (Pi/T-joints),
    - c) Rotational or torsional mode (super-charger rotor), Testing at Eaton.
    - Also, evaluate re-assembly and performance after assembly for each mode.
- **E. Dissemination of results**

Next: What is Graphene and Why?

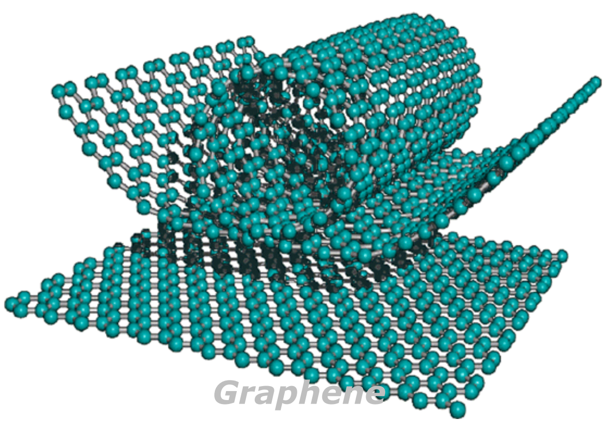
Graphene Nanoplatelet & Carbon Nanotube

A. Processing, Material Development and Optimization of Active Adhesive

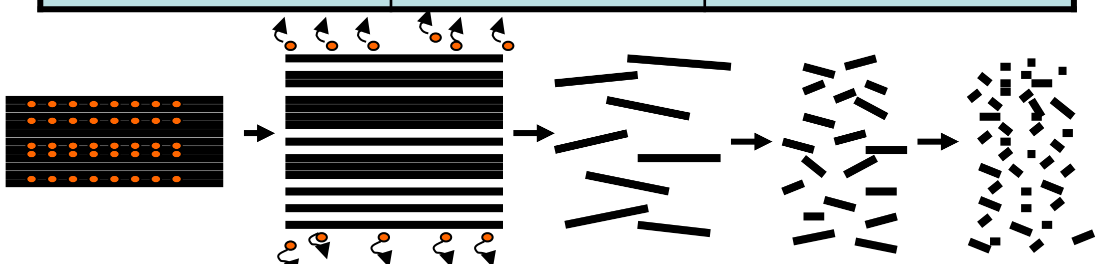


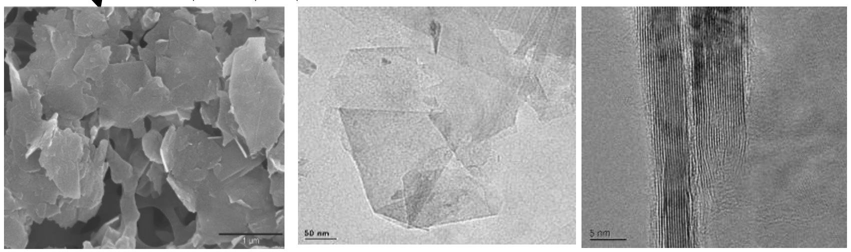
Single and Multiwall Carbon Nanotubes

	Carbon Nanotube	*Graphene NanoPlatelets*
PHYSICAL STRUCTURE	Cylinder- ~1nm X 100nm	Platelet-~1nm X 100nm
CHEMICAL STRUCTURE	Graphene (chair, zigzag, chiral)	Graphene
INTERACTIONS	π - π	π - π
TENSILE MODULUS	1.0-1.7 TPa	~1.0 TPa
TENSILE STRENGTH	180 Gpa	~(10-20 GPa)
ELECTRICAL RESISTIVITY	~ 50 x 10^{-6} Ω cm	~ 50x10^{-6} Ω cm $\parallel$ ~ 1 Ω cm$\perp$
THERMAL CONDUCTIVITY	3000 W/m K	3000 W/m K $\parallel$ 6 W/m K $\perp$
COEF THERMAL EXP.	-1 x 10^{-6}	-1 x 10^{-6} $\parallel$ 29 x 10^{-6} $\perp$
DENSITY	1.2 – 1.4 g/cm³	~2.0 g/cm³



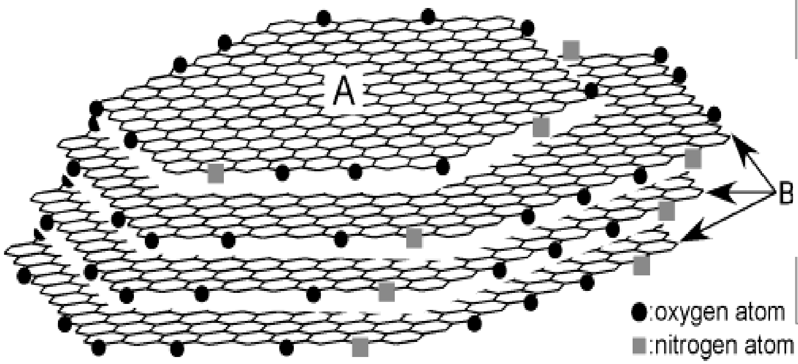
Graphene

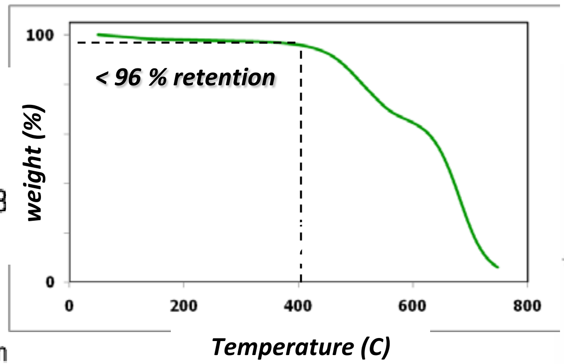


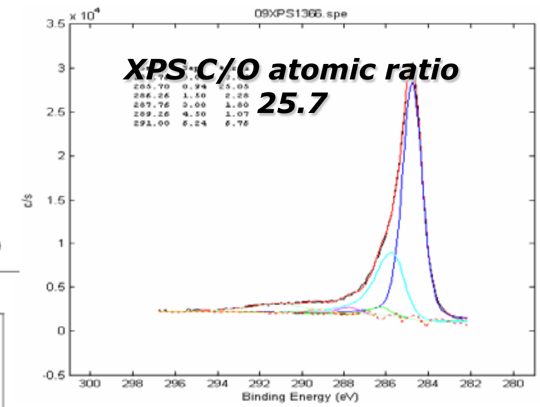


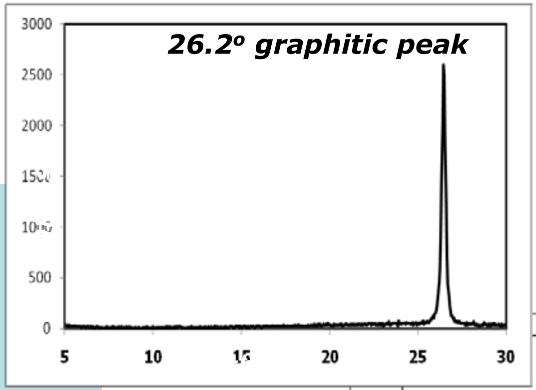
‘Quality’ of Graphene Nanoplatelet (GnP)

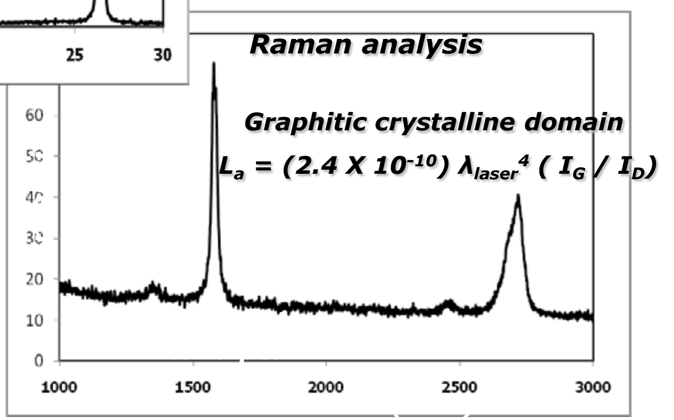
- **A. Processing, Material Development and Optimization of Active Adhesive**







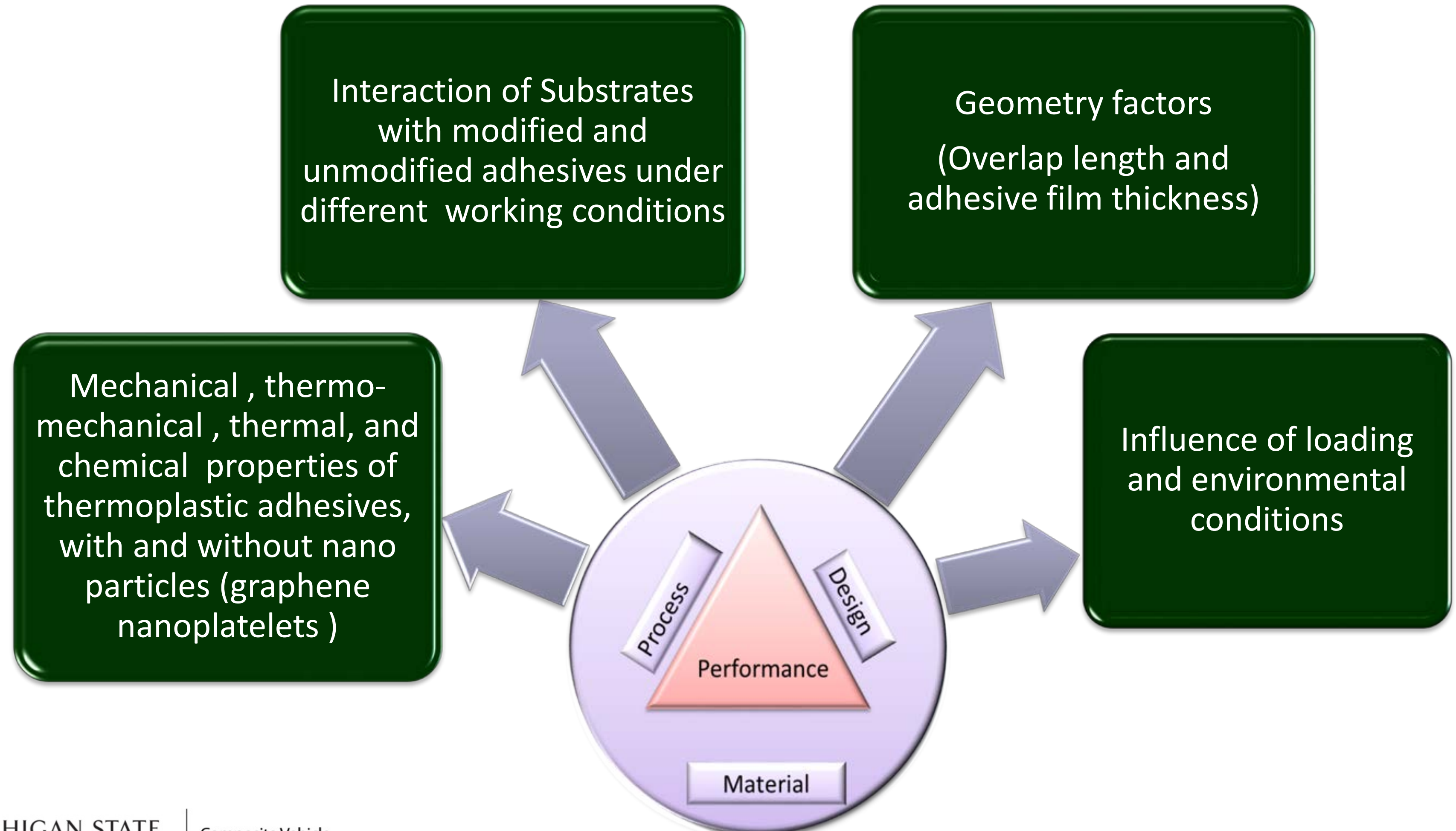




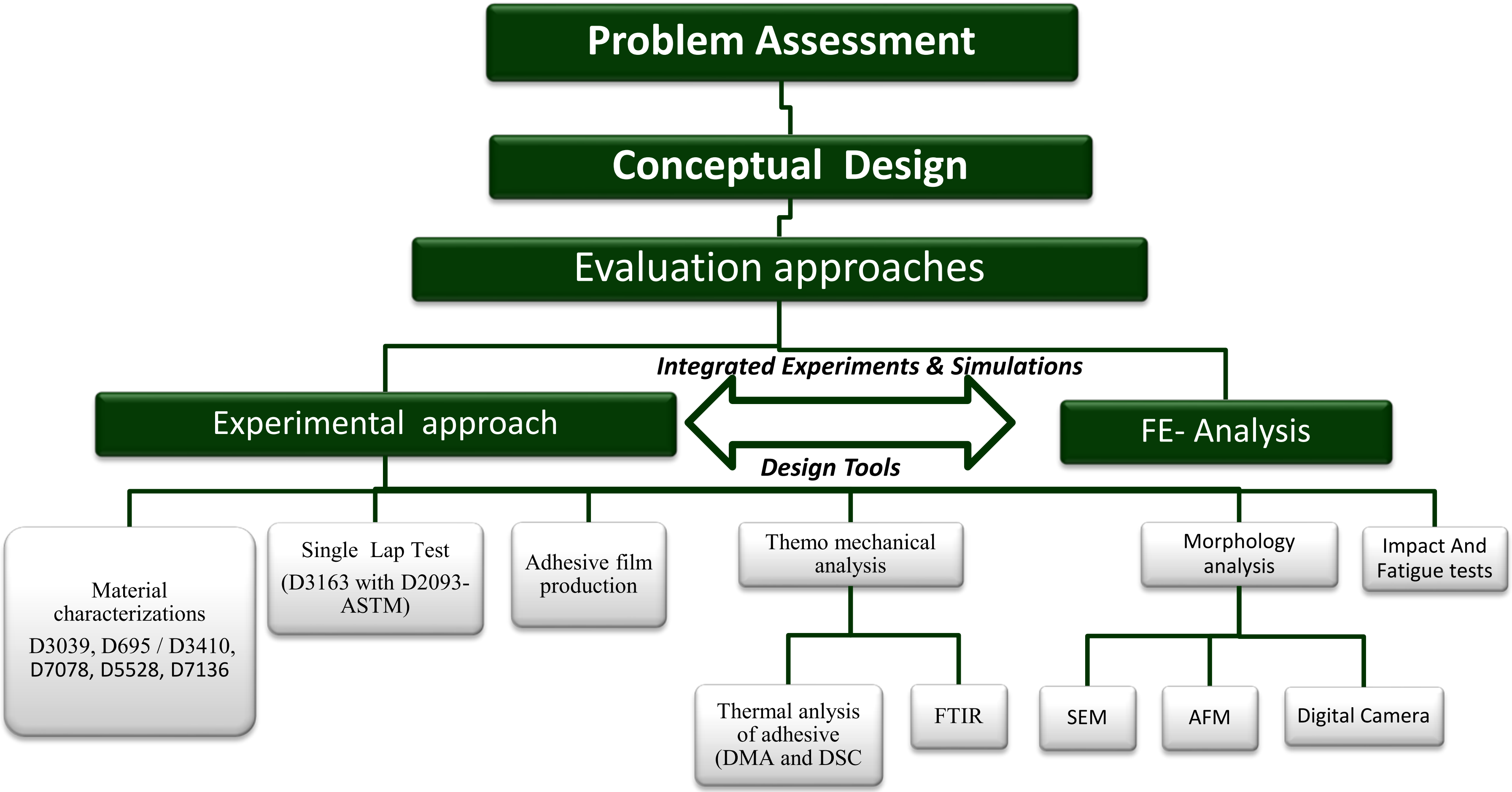
Layers can be intercalated and exfoliated into platelets with high aspect ratios
(dia ~0.3μ to 50μ and t~ 1nm to 5nm)
Basal Plane is hydrophobic
Functional groups at GnP edges
Covalent bond formation at edge sites
Surface areas from 100m²/g to 750m²/g
Some reduction in properties from monolayer graphene to few layer graphene
Inexpensive to produce (~$10-15/lb)

Design Factors Considered to Achieve ‘Active Adhesives’

- ***The performance of active adhesives is dependent on manufacturing process, material properties, application type/area, and design methodology.***



Work Plan and Approach



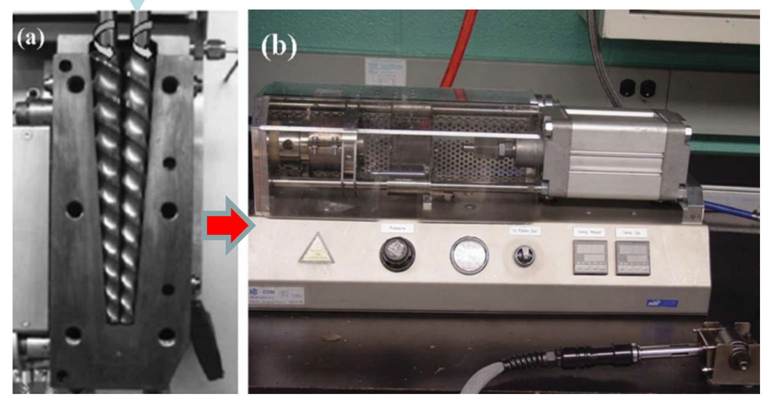
A detailed Design of Experiments was performed to determine the optimum of concentration of nano graphene platelets that gives high adhesive strength and rapid temperature response.

Progress: Processing of Active Adhesives

Nylon/6	
Chemical base	*PA 6 Extrusion grade*
Cure mechanism	*Physical hardening*
Density	*1.14 g/cc*
Viscosity at 180°C	*225cm^3/g approx*
Vicat Softening temperature	*200°C*
Application temperature	*220 – 260°C*
CTE, linear	*80µm/m-°C*

xGnP-5	
Chemical base	*Graphene*
xGnP-5 nanoplatelets diameter	*5µm*
xGnP-5 nanoplatelets thickness	*~10-20nm*
Density	*g/cc*

Nylon-6
+
Graphene (GnP-5)

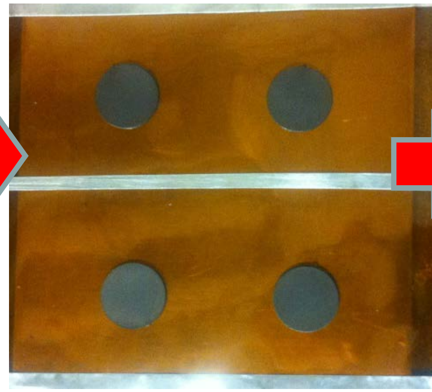


(a) DSM Micro 15cc Compounder, (vertical, co-rotating, twin-screws microextruder); (b) A Daca Micro injector.

Progress: Processing of Active Adhesives

- **Film and specimens production**

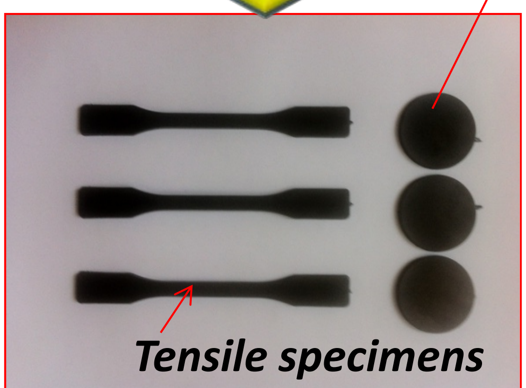
a)DSM Micro Compounder,&
A Daca Micro injector

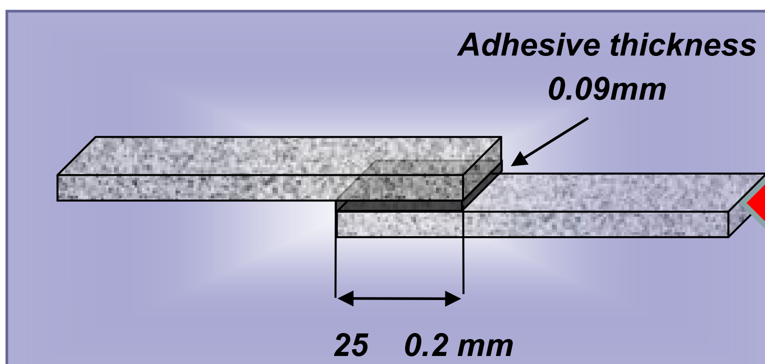


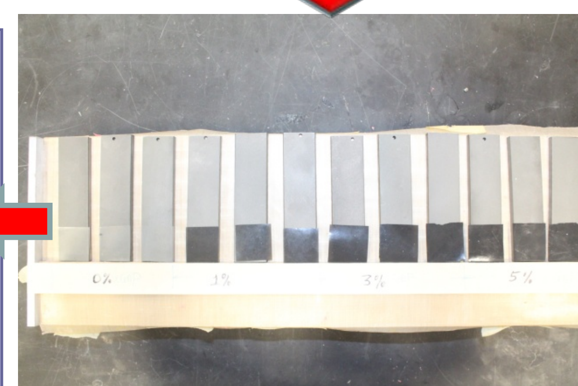
Manufactured Disks

Pressing machine

xGnP modified Nylon-6



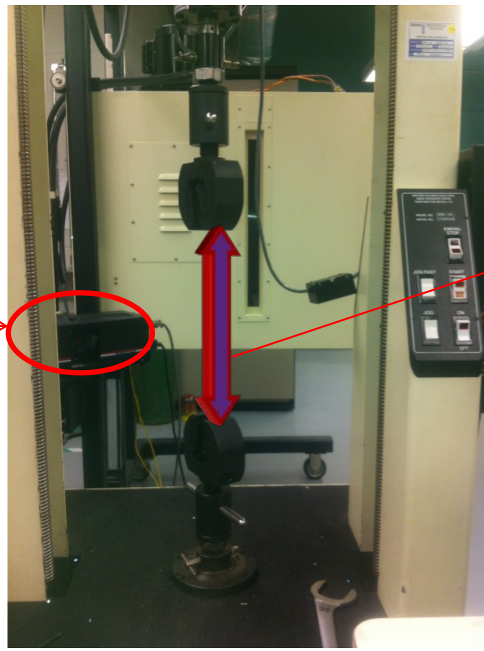


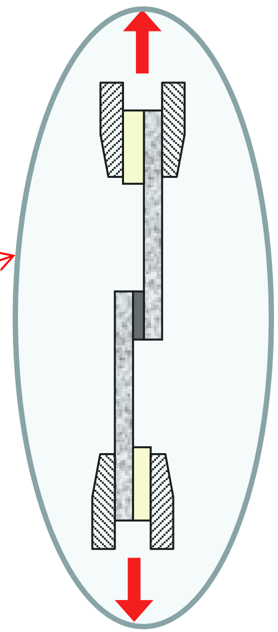


Progress: Experimental Testing and Setup(s)

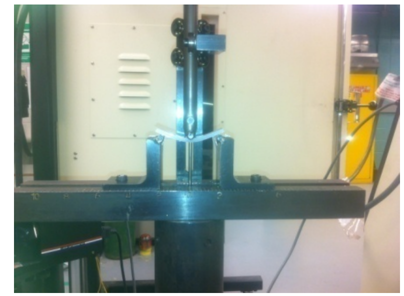
- **Pristine and xGnP modified Nylon-6 characterization was performed with Screw driven testing machine (Universal testing system, UTS).**

Laser Extensometer

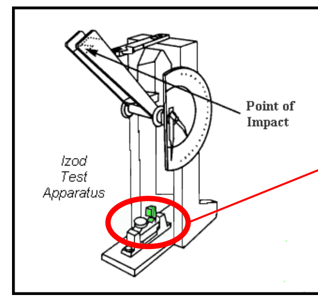


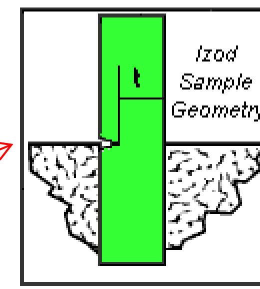


Crosshead velocity



Flexural impact

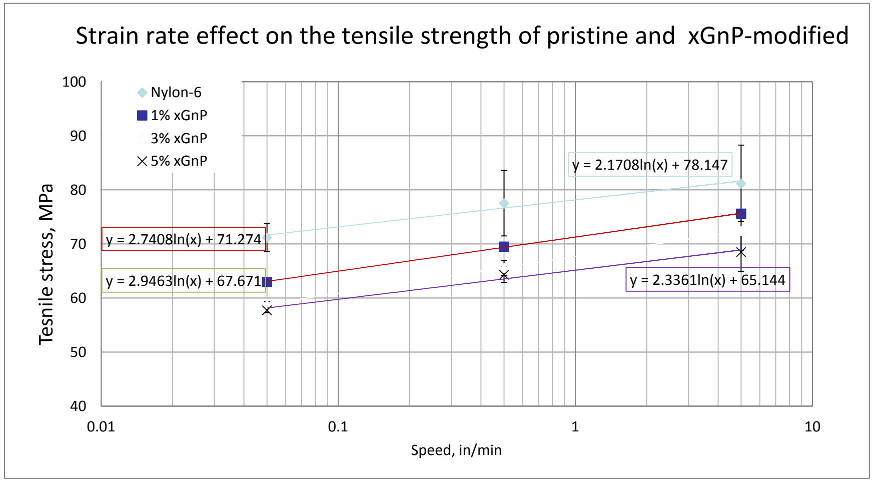


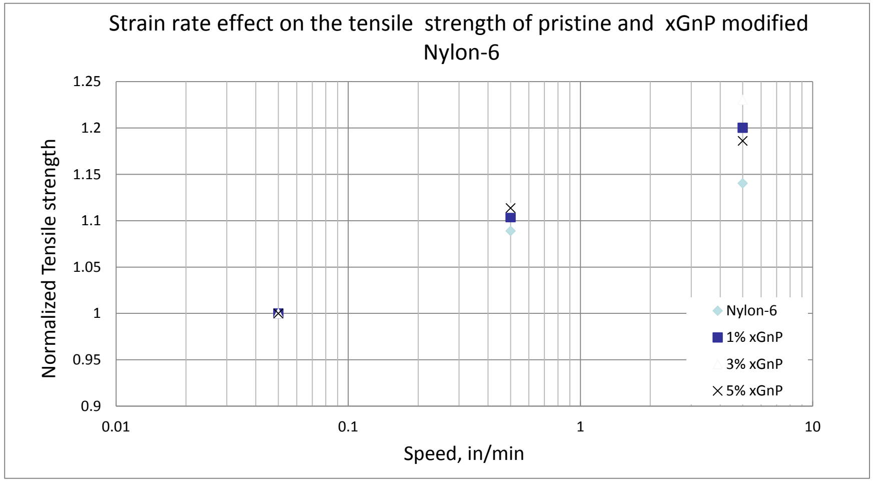


Izod impact

- **Five specimens for each types of standards were tested to obtain the tensile strength and Young's modulus (Ex), according to ASTM D760.**
- **Laser extensimeter was used to measure the axial strain.**
- **Flexural and Impact tests for each material configuration were also performed per ASTM D790 and D256, respectively.**

Interim Technical Accomplishments & Progress



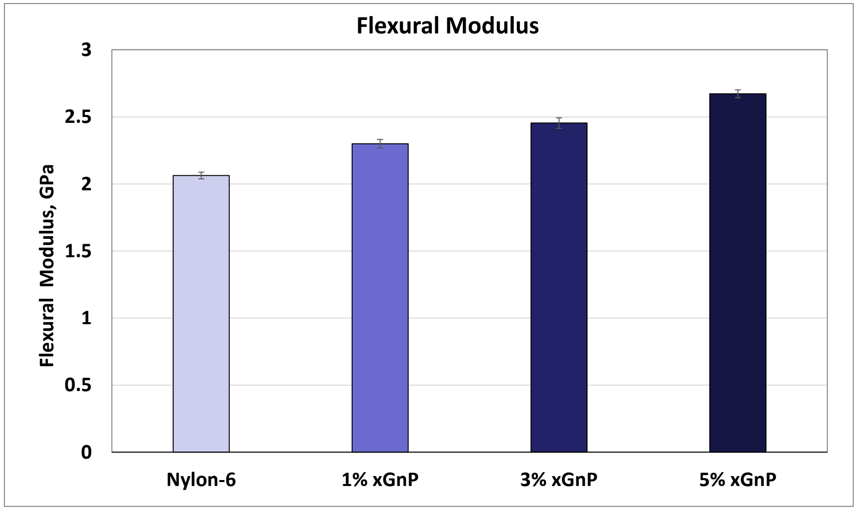


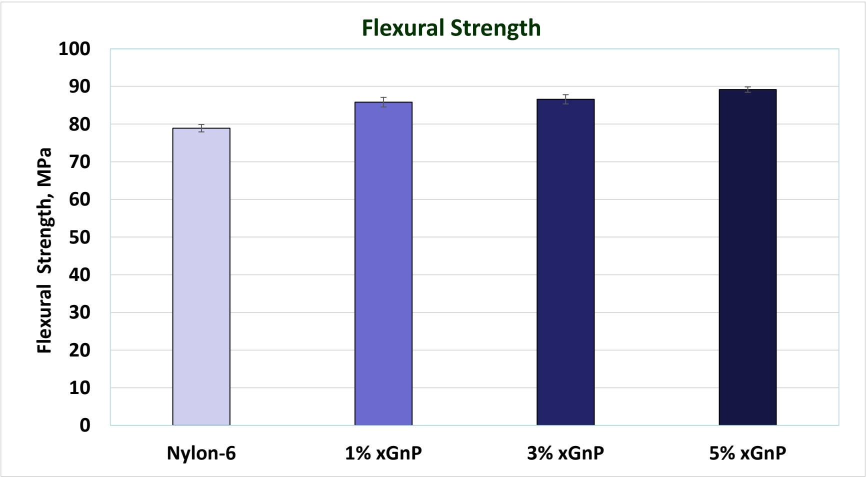
➢ ***Generally, presence of GnP in Nylon-6 was found to decrease tensile strengths.***

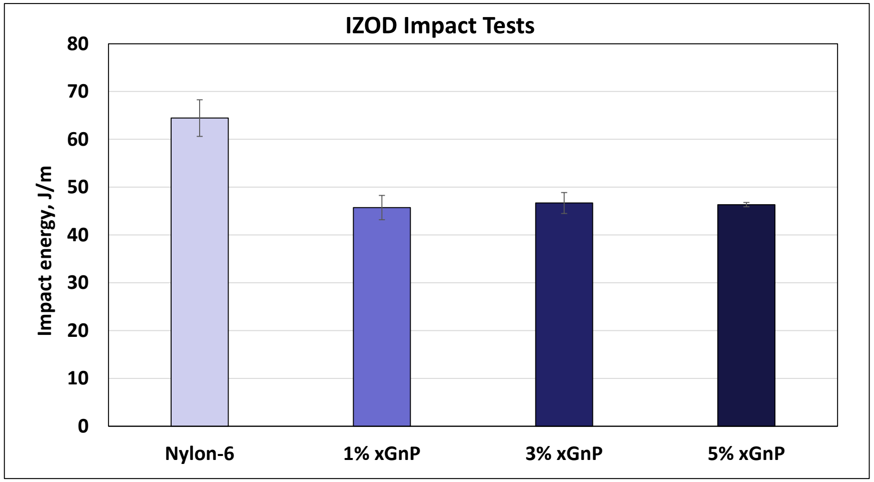
➢ ***However, presence of GnP in Nylon-6 has shown improved strength at higher strain rates relative to pristine Nylon-6. Promising for crash-related applications***

➢ ***Functionalization of GnP in progress to increase chemical compatibility with host polymer will increase the tensile properties***

Interim Technical Accomplishments & Progress





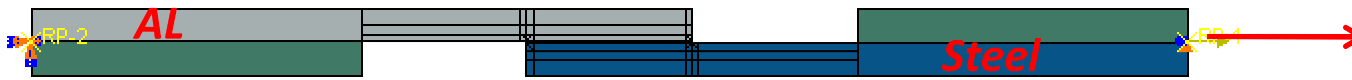


- ***For 5% of xGnP, the flexural modulus Nylon-6 was improved by more than 30% while strengths were improved by more than 10%.***
- ***As expected, impact energies reduced with increasing GnP content***
- ***Functionalization of GnP to increase chemical compatibility with host polymer will increase the tensile properties***

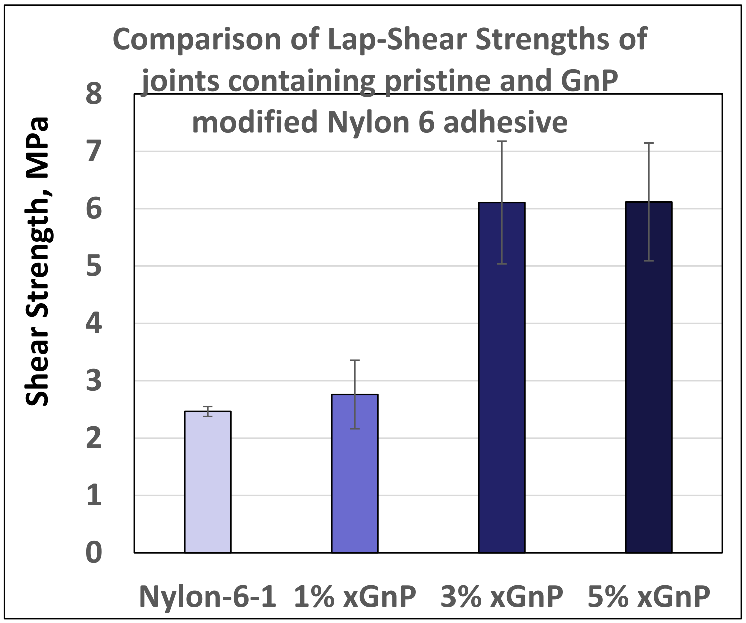
Interim Technical Accomplishments & Progress

➢ ***Single Lap-Joint (SLJ) Tensile Shear Tests***

Fixed end



Applied load

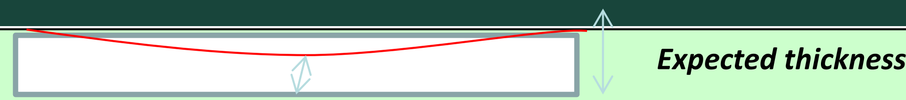


- ***Preliminary results reveal adhesive joint strength improvement with increase in GnP content. Further experimental tests are currently in progress to obtain statistically significant data***
- ***3% GnP SLJ showed comparable shear strength with 5% GnP SLJ.***
- ***For all material cases, dominant failure mode was combined cohesive and interfacial failure.***
- ***As expected agglomeration of GnPs was more pronounced at high concentrations***

- ***For GnP modified nylon-6, the SEM image showed clusters of GnPs with less than ten micrometer diameters; suggesting a poor interfacial adhesion with matrix,***
- ***SEM observations revealed that the fracture surfaces of GnPs were smooth.***
- ***Functionalization of GnP to be compatible with host polymer will enhance mechanical properties and improve the degree of exfoliation***

Challenges / Barriers and Future Work

- **CHALLENGES:**



- Maintaining constant film thickness; SOLUTION: Strategic use of spacers, mesh such that inherent adhesive properties are not altered.
- Improve GFRP adherend properties to withstand high temperatures (beyond melting points of thermoplastic adhesive) for repeatable bonding.

- **FUTURE WORK:**

- REST of Budget Period -1 (until 12/14):
  - Activation studies: GnP+ Microwave Interaction
  - Optimal GnP content for multi-functionality
  - Structural Behavior of Multi-material Joints

- Budget Period -2 (01/15-12/15):
  - Low-Cost Manufacturing of composite Adherends
  - NDE + Damage Induced Behavior, Repair and Re-assembly
  - Structural Behavior Evaluation

- Budget Period-3 (01/16- 09/16)
  - Development of Robust Simulations (multi-scale Analysis) and Design Tools
  - Proof-of-Concept with Large-scale Industrial Applications and Dissemination of Results

Summary

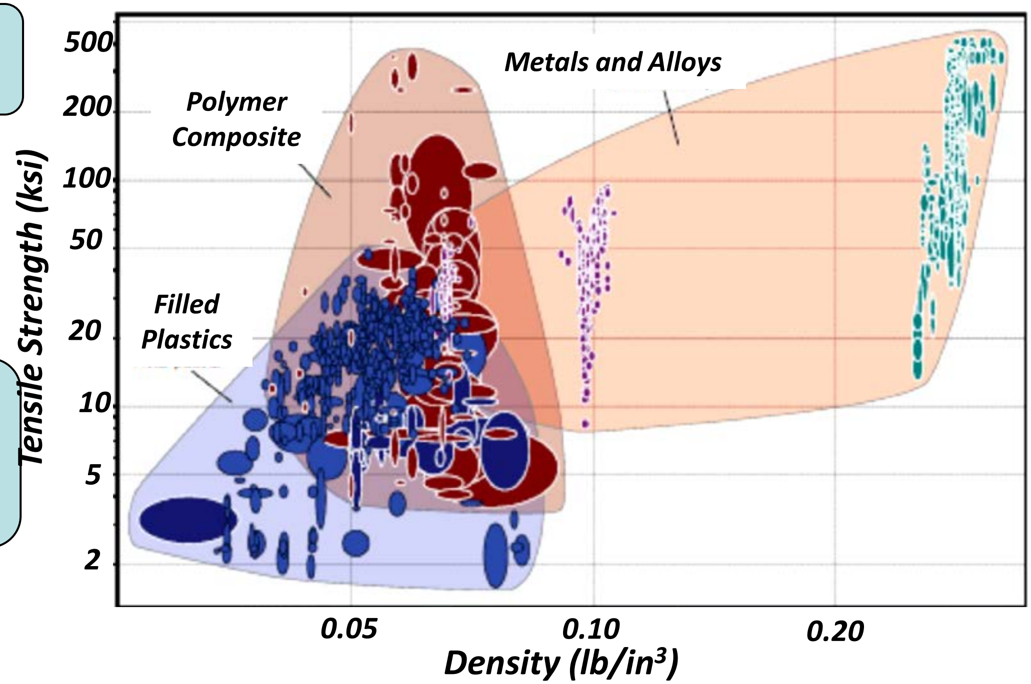
- **RELEVANCE:**
  - **Joining & Assembly: Multi-material Joints that inherit the benefit of both bonded (lightweight) & bolted (re-assembly+repair) joints through 'active,' 'reversible,' adhesives.**
- **APPROACH:**
  - **Reinforcement of thermoplastic adhesive with novel graphene nano-platelets (GnP) and to use GnP/microwave-interaction for 'targeted heating of adhesive' thereby allowing ease of repair and re-assembly**
  - **An Integrated Experimental & Simulations based approach that eliminates the trial-and-error approach is adapted. Robust design tools are also developed.**
- **TECHNICAL ACCOMPLISHMENTS**
  - **Successfully Developed Novel GnP reinforced TP Adhesives. Key parameters identified.**
  - **Structural Properties of Adhesives and Resulting Multi-material Joints completed.**
  - **Dissemination of Results: Conference Presentation, ASC 2014, Accepted.**
- **Partners / Collaborations: Eaton Innovation Center, MI.**
- **FUTURE WORK:**
  - **Activation / Re-Assembly Studies**
  - **Low-Cost Manufacturing**
  - **NDE+Development of Design Tools**
  - **Proof-of-Concept on Large-scale Industrial Applications**

Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair and Assembly

TECHNICAL BACKUP SLIDES

RELEVANCE / MOTIVATION : WHY COMPOSITES?

- **Offer Unparalleled Weight Savings**
- **Low Density, Improved Strength Better energy Absorption and Increased Safety.**
- **Create Value through Consolidation of Parts - JOINING**
- **U.S. Department of Energy is putting considerable efforts in light-weighting technologies.**

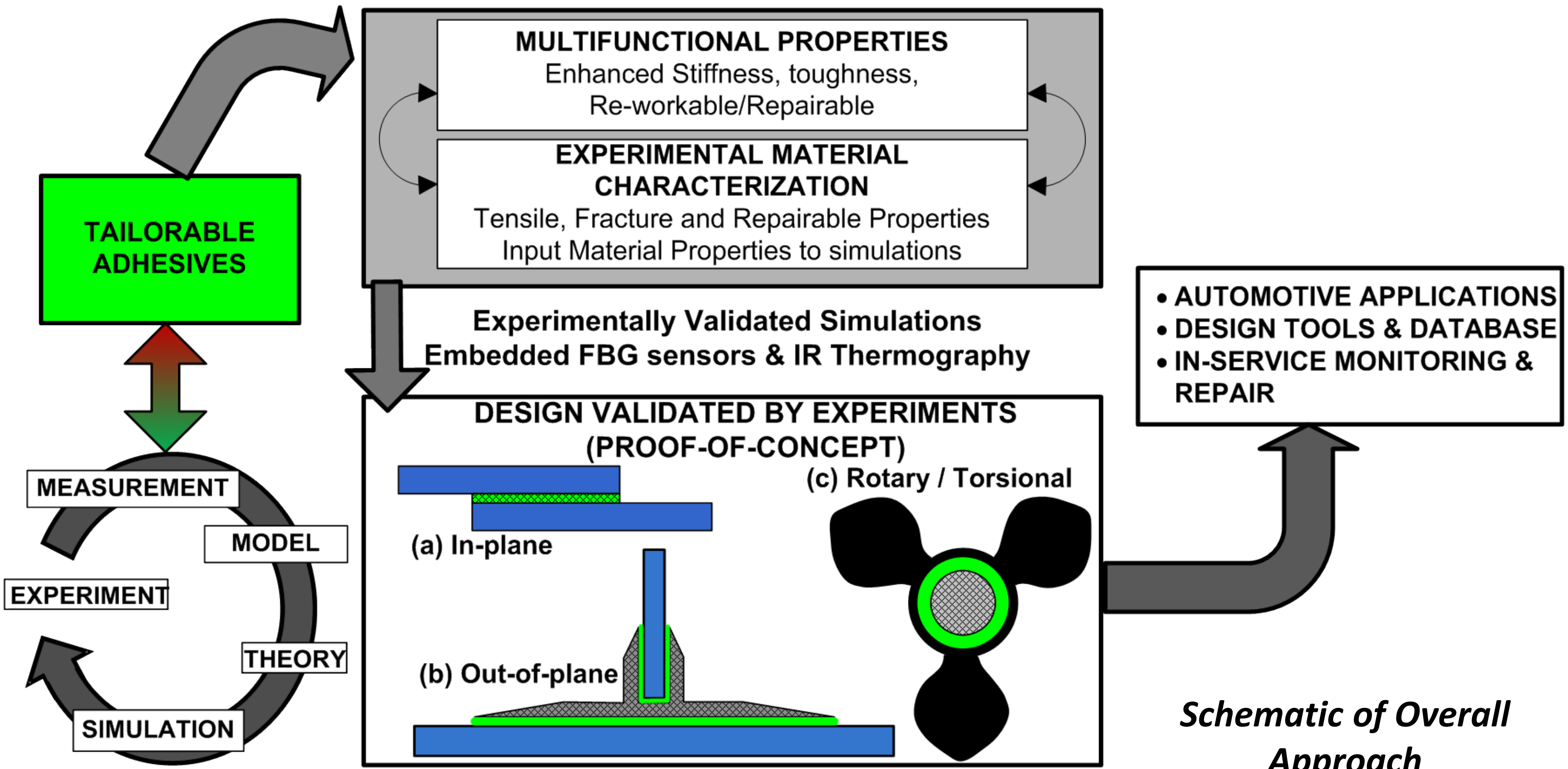


Tensile strength versus density for filled plastics, polymer composites, and metals and metal alloys
Courtesy: Granta Design / ACC RoadMap - 2014

- ***U.S. DOE has identified four key challenges for use of composites for light-weighting technologies***
  - **Cost of Materials**
  - **Cost of Manufacturing**
  - **Dissimilar Material Joining**
  - **Modeling/Simulations and Database Creation**

Objective(s) & Approach

- **GLOBAL APPROACH**

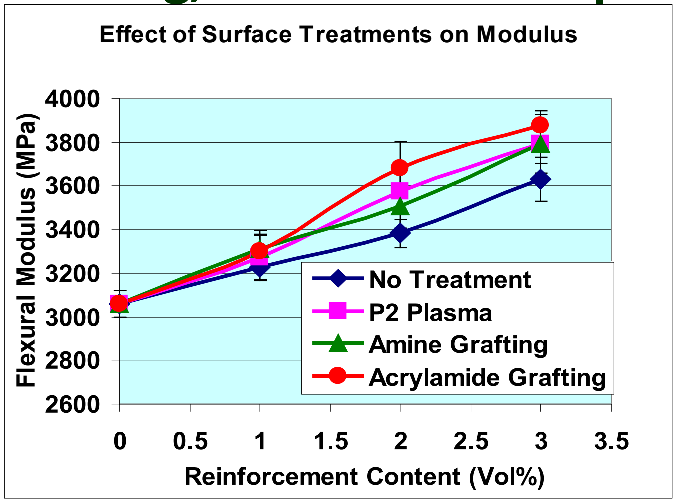


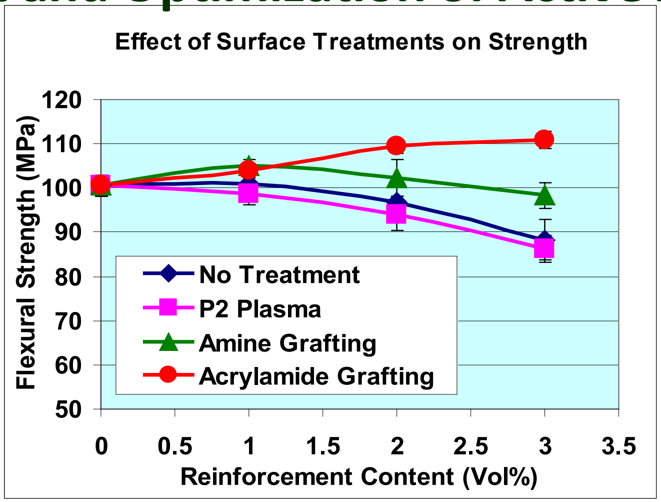
Schematic of Overall Approach

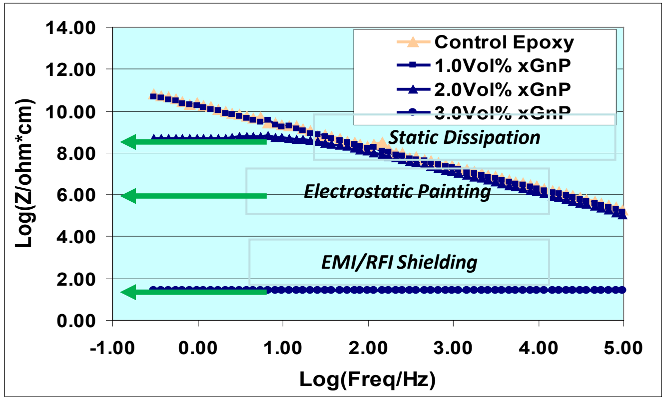
- Most structural joint development focuses solely on in-plane behavior. This work evaluates a) in-plane, b) out-of-plane and rotary/torsional joint

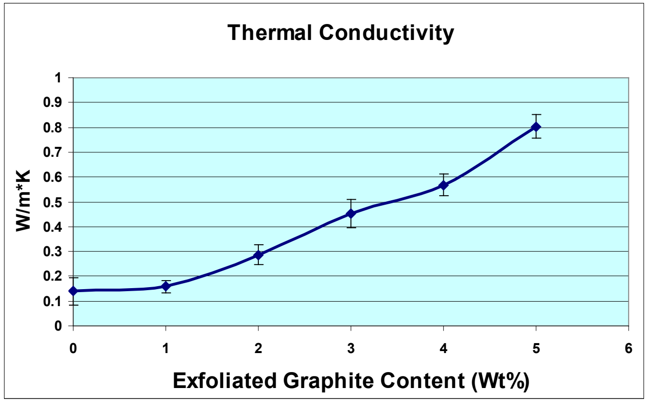
GnP/Epoxy Nanocomposite Flexural Properties

- **A. Processing, Material Development and Optimization of Active Adhesive**









~100m^2/g GnP

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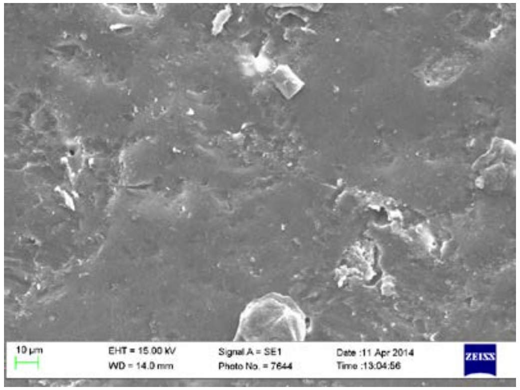
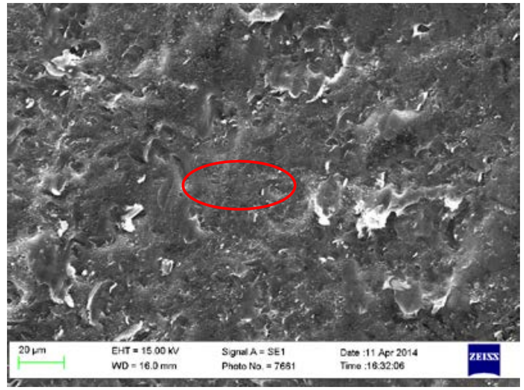
Interim Technical Accomplishments & Progress

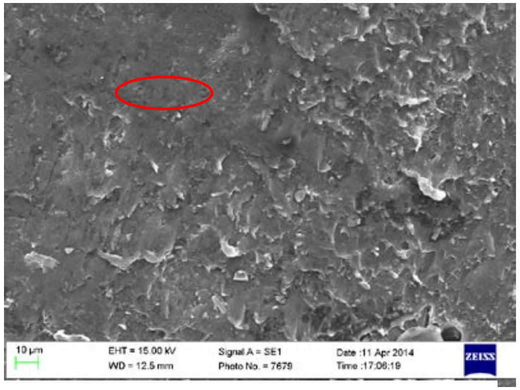
➢ ***SEM Fracture Surface observations***



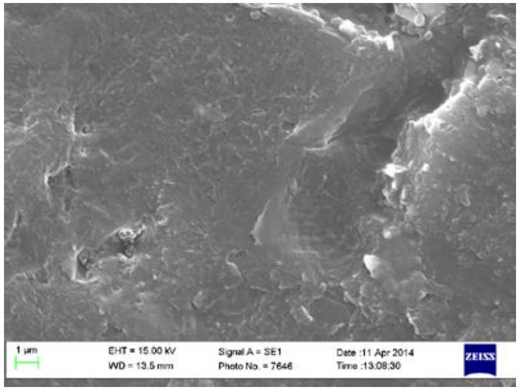
0% GnP, 500X



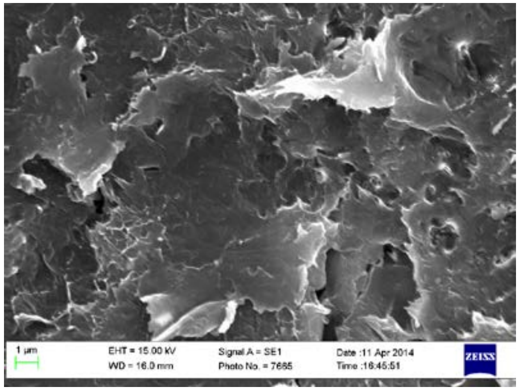
3% GnP, 500X



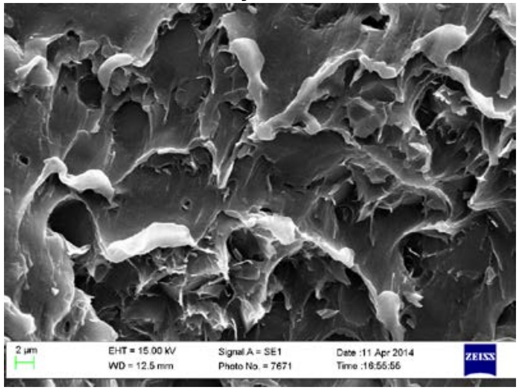
5% GnP, 500X



0% GnP, 5000X



3%xGnP, 5000X



5%xGnP, 5000X

➢ ***Study of fracture surfaces can help understand the crack growth and fracture mechanisms***

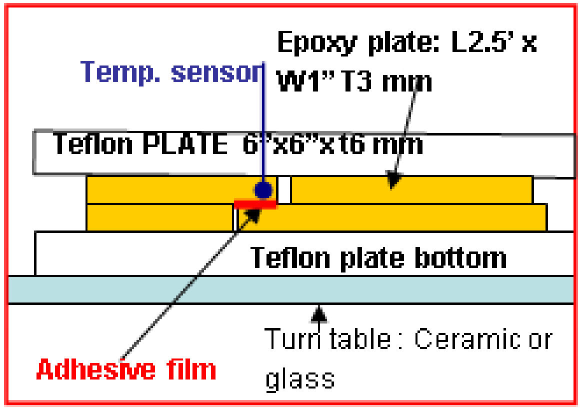
➢ ***A smooth surface is attributed to a brittle material, while a rough surface is attributed to a tougher material. GnP introduced resistance to crack growth leading to rougher surfaces***

Interim Technical Accomplishments & Progress

- Tensile tests were performed on Pristine and GnP-modifed Nylon-6. However, based on the properties of the materials used, commonly prescribed crosshead velocity was not achieved that yields a rupture within ½ to 50-min test time.
- Hence, three testing speeds, namely, 0.05, 0.50, and 5.00 in./min were taken to evaluate the tensile strength of the Pristine and xGnP-modified Nylon-6.
- For flexural and Izod impact tests, single crosshead speed and impact velocity, respectively, were chosen according to ASTM standards.
- 'Active Adhesive' films were manufactured using a press @ pressure of ~82MPa.
- The adhesive film thickness used for single lap joints was 0.09 mm
- The steel-aluminum single lap joints with adhesive films were heated inside a convection oven for 260 °C. The temperature was held for about 10 minutes and later cooled.

Preliminary Results- Lap-Shear Tests

- **A. Processing, Material Development and Optimization of Active Adhesive**



Variables to be investigated:

- ***Thermoplastic Adhesive***
- ***GnP content***
- ***GnP Size***
- ***GnP Surface Chemistry***
- ***Pressure***
- ***Temperature***

GnP-15 6wt%/nylon-6